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POLYNUCLEAR AROMATIC CONTENT OF HEAVY DUTY DIESEL ENGINE EXHAUST GASES

R. S. Spindt

Gulf Research and Development Company

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7. Author(s)

R. S. Spindt

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Gulf Research & Development Company
P. O. Drawer 2038
Pittsburgh, Pennsylvania 15230

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ON

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For Period
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By
R. S. Spindt
Gulf Research & Development Company
P. O. Drawer 2038
Pittsburgh, PA 15230

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ABBREVIATIONS

APRAC - Air Pollution Research Advisory Committee

Anth - Anthracene

BaA - Benz(a)anthracene

BaP - Benzo(a)pyrene

C^{14}BaP - Radioactive Benzo(a)pyrene

BeP - Benzo(e)pyrene

BghiP - Benzo(g,h,i)perylene

Chry - Chrysene

DDAD - Detroit Diesel Allison Division

Fluo - Fluoranthene

IO - Isooctane

M-Anth - Methyl Anthracene

PNA - Polynuclear Aromatic Hydrocarbons

Phen - Phenanthrene

Pyr - Pyrene

TLC - Thin Layer Chromatography

V-V - Volume/Volume

PERSONNEL

Supervisory Project Group

Mr. Roger Bascom - Chairman	-	Cummins Engine Company
Mr. C. R. Begeman	-	General Motors Research Laboratories
Mr. D. S. Gray	-	AMOCO Oil Company
Mr. R. J. Hames	-	Detroit Diesel Allison Division, General Motors Corporation
Mr. M. Malbin	-	Shell Development Company
Mr. R. E. Maxwell	-	Environmental Protection Agency
Dr. S. S. Hetrick	-	Mobil Research and Development
Dr. Margaret Griffing	-	Ethyl Corporation
Dr. H. K. Newhall	-	Chevron Research Company
Dr. J. M. Perez	-	Caterpillar Tractor Company

Gulf Research & Development Company Personnel:

Dr. R. S. Spindt	-	Project Manager
Mr. J. C. Mulac, Jr.	-	Senior Project Engineer
Mr. J. G. Berry, Jr.	-	Project Engineer
Mr. M. S. Norris	-	Senior Research Chemist
Mr. E. D. Hill	-	Research Chemist
Mr. E. S. Dorinsky	-	Technician

I. SUMMARY

The first phase of a CRC/EPA sponsored study of polynuclear aromatic (PNA) and phenolic hydrocarbon emissions from diesel engines has been completed by Gulf Research & Development Company. The first year's effort was concentrated on validation of the sample collection and analytical techniques and a survey of the PNA content of U.S. diesel fuels.

A collection system consisting of a precooler, a glass fiber particulate filter, and a Chromosorb-102* trap was used to collect PNA's from diesel exhaust. PNA's are removed from the collection system by solvent washing and soxhlet extraction, concentrated, and analyzed by thin layer chromatography. Total phenols are analyzed by the 4-amino-antipyrene procedure.

Attempts to validate the sample collection system using C^{14} tracers were not successful. It is hypothesized that PNA's injected into the exhaust (i.e., tracers) are largely destroyed by reactions with other exhaust components, while engine-generated PNA's on or within soot particles survive these reactions. Radio tracers also indicate that PNA-destroying reactions occur even after collection and extraction from the sample system. Similar losses of PNA's do not occur with synthetic exhaust.

The fuel analyses showed that ASTM 1-D diesel fuels are nearly free of PNA compounds. PNA levels in ASTM 2-D diesel fuels ranged from near zero to values that reach the average concentration reported in motor gasolines.

*Chromosorb-102 is a registered trademark of Johns-Manville, Inc.

Work has been started to determine the effect of operating conditions on PNA emissions and to establish the repeatability of the overall procedure. Future work will concentrate on measurement of PNA emissions from other types of diesel engines and on identifying the effects of specific operating conditions, blowby, deposits, lube oil, and fuels.

II. INTRODUCTION

Concern for air pollution has shifted from major pollution sources, first subjected to control measures, to include those of lesser magnitude as the major sources have come under control. Diesel engine exhaust is still a minor factor in pollution in the United States. But because the diesel engine produces both smoke and odor in the exhaust, attention to this problem area is justified.

Polynuclear Aromatic Hydrocarbons (PNA) do not appear to occur naturally in the environment but have been associated with combustion processes.[1,2]* Ray and Long[1] state that PNA is associated with soot formation and inefficient combustion. Bailey, et al[2] states that PNA in diesel engines is associated with overfueling.

A Public Health Service[3] study indicated that hand fired coal burning combustion sources are the most important source of BaP emissions in the United States. Much lower emissions were estimated for all other combustion sources including motor vehicles.

An important investigation of the automotive vehicle contribution to BaP levels in the atmosphere has been completed by Colucci and Begeman.[4] They showed that vehicular contributions to total PNA levels could account for between 5 and 42% based on correlations with lead measurements. In another study, these authors[5] showed that BaP in the fuel can survive the combustion processes in a gasoline engine (up to 36%). Gross[6] in a study for the CRC-APRAC, showed that PNA emissions from gasoline engines were influenced by (a) emission control systems, (b) PNA in fuel, and (c) oil consumption rate.

*Numbers in parenthesis designate References at end of report.

As a result of the extensive PNA studies that have been made on the gasoline engine and the relatively little work that has been done on the diesel engine, the EPA and CRC-APRAC, in the fall of 1972, agreed to fund a project to investigate PNA in diesel exhaust gases. The project was awarded to Gulf Research & Development Company with a starting date of June 29, 1973.

The scope of work for this project envisioned a two-year program with specific items clearly spelled out. The eight items included are as follows:

1. Demonstrate and validate the sample collection and analytical techniques.
2. Survey a number of fuels and select a baseline fuel.
3. Measure PNA emissions from selected (7) engines.
4. Measure PNA emissions by operating mode.
5. Determine PNA emissions with fuels of high and low PNA content.
6. Evaluate deposit effects on PNA emissions.
7. Determine the accumulation of PNA in the oil.
8. Evaluate effect of exhaust gas recirculation.

Only the first four items were to be included in the first year's contract. Tasks 3 and 4 were not completed under this contract due to the increased expenditure required to resolve problems encountered in Task 1.

III. EXPERIMENTAL

A. Analytical Procedures

We chose to determine polynuclear aromatic hydrocarbons (PNA) and phenols by a separation technique that includes liquid solid column chromotography and thin layer chromotography. Details of the procedures are given in Appendix A.

It was anticipated that the engine exhaust sample would be collected using a filter and a chromosorb-102 adsorption trap.(7) This material is known to adsorb hydrocarbons readily. Simple elution with benzene was expected to recover the PNA quantitatively from the chromosorb for further separation.

B. Bench Studies to Validate Sampling Techniques

To test the efficiency of the proposed trapping system for PNA, a heated gas flow system was constructed as shown in Figure 1. The construction of the sampling trap is shown in Figure 2. Air or nitrogen gas at 3 CFM (5 m^3/hr.) heated to an exit temperature of 350°F (177°C), was spiked with benzo(a)pyrene using a motor driven syringe. Five μg Bap in 1 ml. of isooctane was introduced into the gas stream over a 2-hour period, except for runs B8-10.

Table 1 lists the results of these tests for several operating conditions.

FIGURE 1

SYSTEM FOR VALIDATING PNA COLLECTION EFFICIENCY

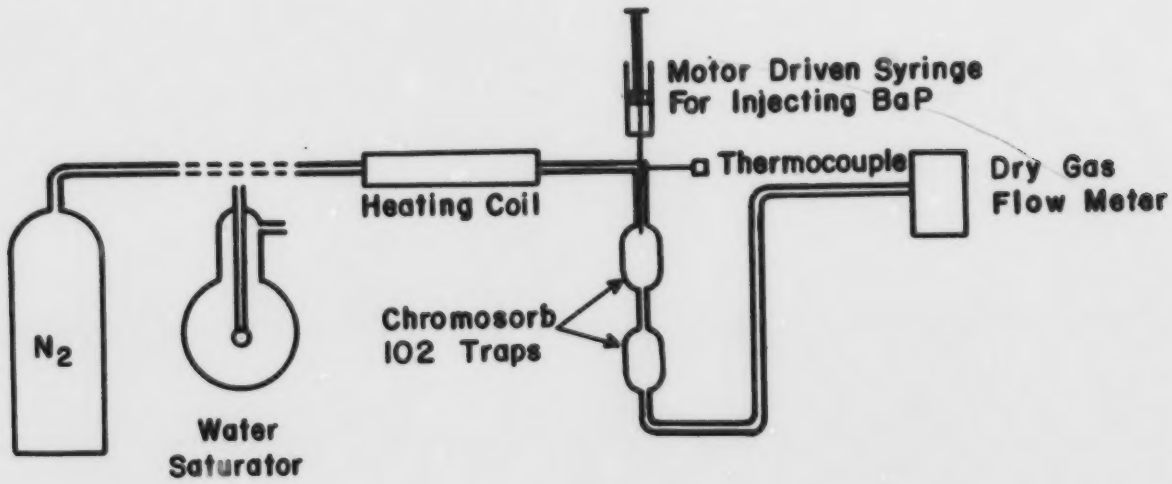


FIGURE 2

CHROMOSORB 102 TRAP

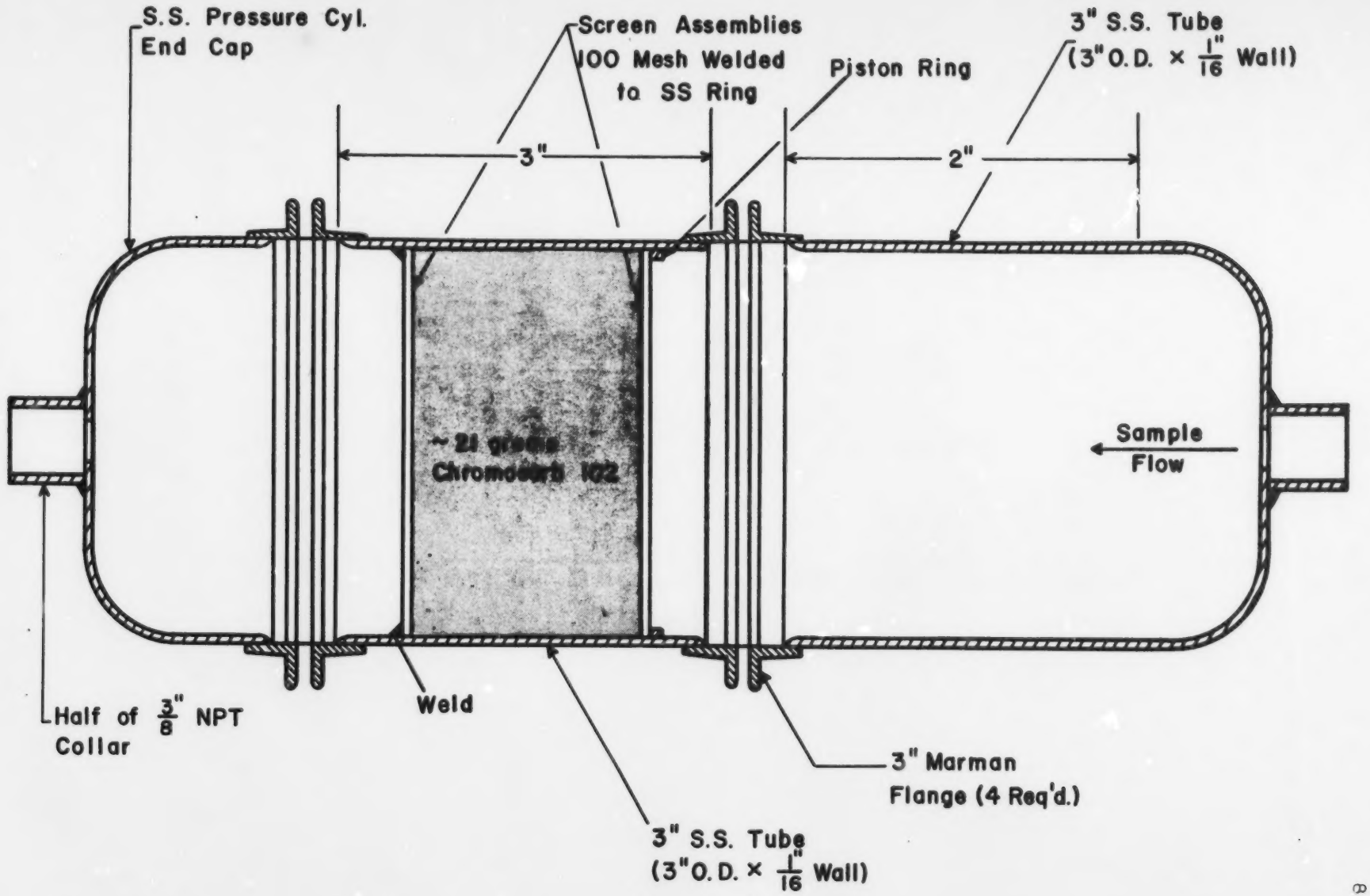

S.S. Pressure Cyl. End Cap
Screen Assemblies 100 Mesh Welded to SS Ring
Piston Ring
3" S.S. Tube (3" O.D. × 1/16 Wall)
3"
2"
~ 21 grams Chromosorb 102
Sample Flow
Half of 3/8" NPT Collar
Weld
3" Marman Flange (4 Req'd.)
3" S.S. Tube (3" O.D. × 1/16 Wall)

TABLE 1

MEASUREMENT OF BaP RECOVERY USING CHROMOSORB-102

Test	Gas Temp.(1)	Added Components	Carrier Gas	Recovery Efficiency % BaP	Phenol
B-1	300°F		N_2	89.	-
B-2	300°F		N_2	89.	-
B-3	300°F	Water Vapor	N_2	74.	-
B-4	300°F	Water Vapor	N_2	85.	-
B-5	350°F	Water Vapor	N_2	76.	-
B-6	350°F	Phenol in IO + Water Vapor	N_2	90.	0
B-7	350°F	m-Cresol in IO + Water Vapor	N_2	96.	23% (in water trap)
B-8	350°F	Preload trap with 5 ug BaP	Air	91.	-
B-9	350°F	Preload trap	Air + 720 ppm NO	87.	
B-10	350°F	Preload trap inject 1 ml. ether + diesel fuel (10%)	Air + 900 ppm NO	85.	

(1) Temperature measured at BaP injection point.

In each case, a second chromosorb trap was installed in the system but no BaP was ever found on it. Therefore, Chromosorb-102 is an excellent scavenger for BaP. The temperature of 350°F (177°C) was chosen because at lower temperature, some of the BaP is found in the lines. A recovery of 86% is quite satisfactory.

Phenol or m-cresol at 100 mg/ml was added with the BaP in two experiments. In neither case, did the presence of these compounds interfere with the recovery of BaP.

The three runs with air as the carrier gas showed that no BaP is flushed from the Chromosorb-102 trap. However, the addition of NO to the air seems to indicate a possible degradation of the recovery. Since these runs were all of short duration (15 minutes), it is possible that longer exposure would have increased the loss.

In these experiments, the syringe, lines and traps are separately washed with benzene and the separate solutions concentrated with 1 ml hexadecane. The final hexadecane solution was then analyzed using ultraviolet spectroscopy. Since only one PNA was present, no separation technique was required, except when ether and diesel fuel were added.

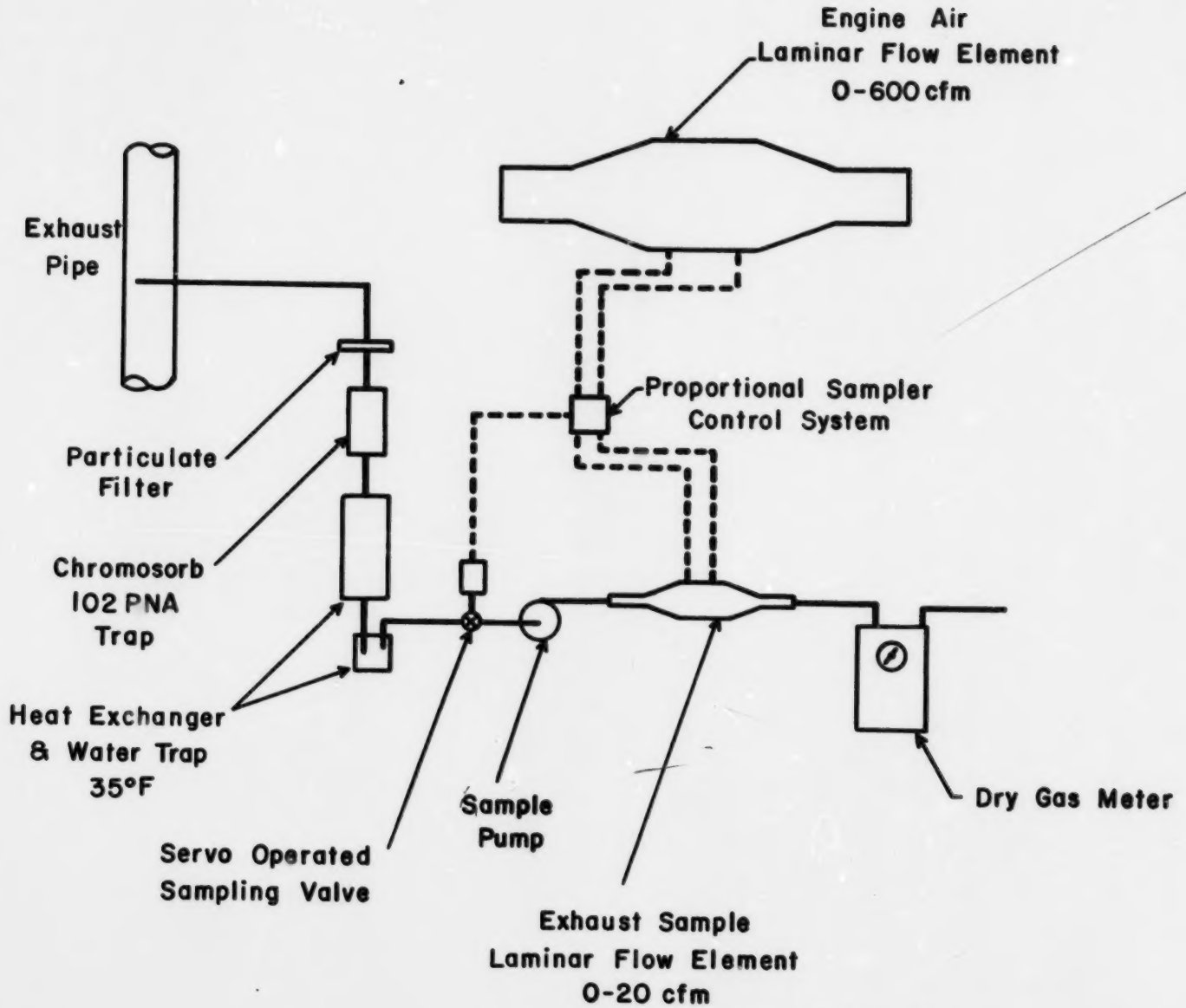
C. Engine Studies

A Detroit Diesel Allison Division (DDAD) model 3-53 automotive engine was available in this laboratory for our initial studies. The engine test cell instrumentation included equipment for measuring: (1) engine torque and speed, (2) fuel consumption, (3) gaseous emissions (CO, HC, NO, NO_x, CO_2, and O_2), and (4) smoke. The optical portion of the smokemeter was mounted at the end of the exhaust stack approximately 25 feet (7.6 m) from the engine. Two sample probes were installed in the engine exhaust pipe approximately 10 feet (3 m) from the engine. One probe supplied exhaust sample for the standard gaseous emission measurements and the second probe supplied sample for PNA analysis. A variable rate proportional sampler was

modified to permit varying the ratio of sample gas volume to total exhaust gas volume. This alteration allows the use of the device on any size engine. Figure 3 is a diagram of the exhaust sampling system.

Two cycles were specified for evaluation in this work. These cycles are given in the Federal Register[8] in complete detail. Appendix B describes the speed load pattern with time that was used. The 13-mode Federal Cycle for standard exhaust pollutant analysis was used for preliminary studies. This cycle can be sampled at constant flow rate, proportional to the engine exhaust flow because it is a series of steady state conditions. The other cycle is the Federal Smoke Cycle composed of transient acceleration and lugging modes. Since this composite transient cycle must be repeated approximately one hundred times, a DATA-TRAK controller was programmed to duplicate this cycle. This cycle controller with the variable rate proportional sampler makes the collection of a constant fraction of the exhaust relatively easy.

FIGURE 3
PROPORTIONAL SAMPLING SYSTEM



IV. RESULTS

A. Exhaust Sample Collection Developments

Table 2 summarizes the results of tests to analyze the PNA emissions and to evaluate the collection and analysis schemes. All tests were run with the DDAD 3-53 engine. The results have not been corrected for analytical losses.

Runs 1 and 2 show results of PNA collection using a direct filtration procedure (Figure 4-A). These data appear to be remarkably reproducible.

Starting with Experiment 3, various PNA were either injected into the exhaust gas or predeposited on the chromosorb to compare the recovery obtained to that in the bench tests. Heated sample lines were used in Experiments 3 through 5 (Figure 4-B) because work with the bench studies indicated that a temperatue of 350°F (177°C) was needed to ensure that the PNA would be in the vapor phase. Only the injected compounds (or those predeposited on the chromosorb) were isolated.

The failure to recover any BaP in Run 3 was surprising and should have been a warning that heating the sample might be a problem. The maximum temperature at the point of taking the sample from the stack varied, depending on engine operating conditions, from 130 to 850°F (54 to 454°C). Run 4 is a strong indication that BaP is partially destroyed in the sampling system, that is, less than 50% of the injected BaP was recovered compared to the approximately 90% in the bench tests. Run 5 indicates that destruction of BeP can occur and that BaP predeposited on the chromosorb is partially lost. Because, in bench studies, BaP on the chromsorb 102 trap was recovered in 90% yield, the 20% recovered in Run 5 probably means that most of the BaP reacted with constituents in the exhaust gases. Similar loss of predeposited BaP on the chromosorb was observed in Runs 6, 7, and 9.

TABLE I

ENGINE STUDIES OF PNA RECOVERY

Engine DDAD-6-63 - Fuel D-2

Exp. No.	Collection System (Figure No.)	Engine Cycle	Injected Compound cmp	Injected Compound µg	Recovery - µg/Test BaP	Recovery - µg/Test BeP	Recovery - µg/Test BaA	Recovery - µg/Test BghIP	Exhaust Volume Sampled M^3	Remarks
1	Direct Filtration and Chromosorb-102 (4-A)	13-mode	-		0.56	0.66	0.59	5.72	7.50	
2	Direct Filtration and Chromosorb-102 (4-A)	13-mode	-		0.48	0.62	0.86	5.45	7.67	
3	Heated line (350°), Filtration, Chrom.-102 (4-B)	13-mode	BaP	6	0	-	-	-	7.39	Injected over total cycle.
4	Heated line (350°), Filtration, Chrom.-102 (4-B)	13-mode	BaP	4.4	2.58	-	-	-	7.67	Injected during last 10 min.
5	Heated line (350°), Filtration, Chrom.-102 (4-B)	13-mode	BaP BeP(1)	5.27 5	1.11	1.95	-	-	6.34	Injection during Mode 11.
6	Condenser + Filter + Chromosorb-102 (4-C)	13-mode	BaP BeP(1)	2.1 5	2.05	1.5	-	-	6.40	Injection during Mode 10 and 11 (10 min.)
7	Condenser + Filter + Chrom.-102 ($C_{10}H_{34}$ on Filter)(4-C)	13-mode	BaP BeP(1)	4.25 5	1.9	0.37	-	-	6.88	Injection during Mode 6 Condenser water not on.
8	Ammonia injection to determine whether NO is destroyed.								-	No loss of NO_x found.
9	Air dil. (4/1) Temp. 75° + Filtration + Chrom.-102 (4-D)	1800 rpm 1/2 load	BaP BeP(1)	9.11 4.87	1.93	6.82	-	-	6.80	Injection over whole test (rest of runs).
10	Air dilution (4/1) (4-D)	1800 rpm 1/2 load	BaP BeP(1)	9.90 5.73	2.61	4.24	-	-	6.51	
11	Air dilution (4/1) Temp. -20° + filtretion. (4-D)	1800 rpm 1/2 load	C^{14}BeP BeP BeP(1) BeP(1)	6.42 5.97 4.0 5.8	5.58(2) 5.22*(2) 1.62(3)	5.57(2) 5.85(3)	-	-	5.24	
12	Condenser + filter + Chromosorb-102 (4-C)	13-mode	BaP BaA	6.22 5.35	2.26 0.0 (3)	-	1.60(2) 0.0 (3)	-	6.97	
13	Heated line - Stack Sampling Procedure (4-E)	1800 rpm 1/2 load	BaP BaA	6.45 5.47	0.64	-	Trace	-	5.21	
14	Cryogenic (-80°) bath + filtretion + Chrom.-102, heated line. Methanol injected. (4-F)	1800 rpm 1/2 load	BaP BeP	6.69 5.72	3.45	1.62	0	.96	6.80	
15	Cryogenic (-90°) bath + filtretion + Chrom.-102 Methanol injected. (4-F)	13-mode	-		0.16	0.69	0	0.14	7.51	Difficult to recover from glass wool in trap.
16	Cryogenic (-90°) bath + filtration + Chrom.-102 (No methanol.) (4-F)	13-mode	-		0.39	0.23	Trace	0.20	8.30	Difficult to recover from glass wool in trap.
17	Precooler, cryogenic trap, filter (4-F)	13-mode	C^{14}BaP	1.50	0.45 0.24*	0	0	0	7.99	Injection ahead of precooler temp.) 400°F in N_2 stream.
18	Precooler, filtration + Chromosorb-102 (5)	13-mode	-		0.58	0.27	Trace	0.72	6.85	Like #1 and 2.
19	Precooler, filtration + Chromosorb-102 (5)	13-mode	C^{14}BaP	0.98	0.59 0.14*	1.46	1.14	0.30	7.76	Injection after precooler.
20	Precooler, cryogenic trap + filter - Ammoniated Methanol injected. (4-F)	13-mode	C^{14}BaP	1.30	0	0	0	0	7.76	Lost.
21	Precooler, cryogenic trap + filter - Ammoniated Methanol injected. (4-F)	1-Mode	C^{14}BaP	1.36	1.31 0.22*	0.71	1.37	0.56	7.90	Replaced Cu cooling coil with stainless steel.

(1) Compound placed on Chromosorb-102 before starting run.

(2) Recovered from filter and lines.

(3) Recovered from Chromosorb-102.

*Radioactive BaP.

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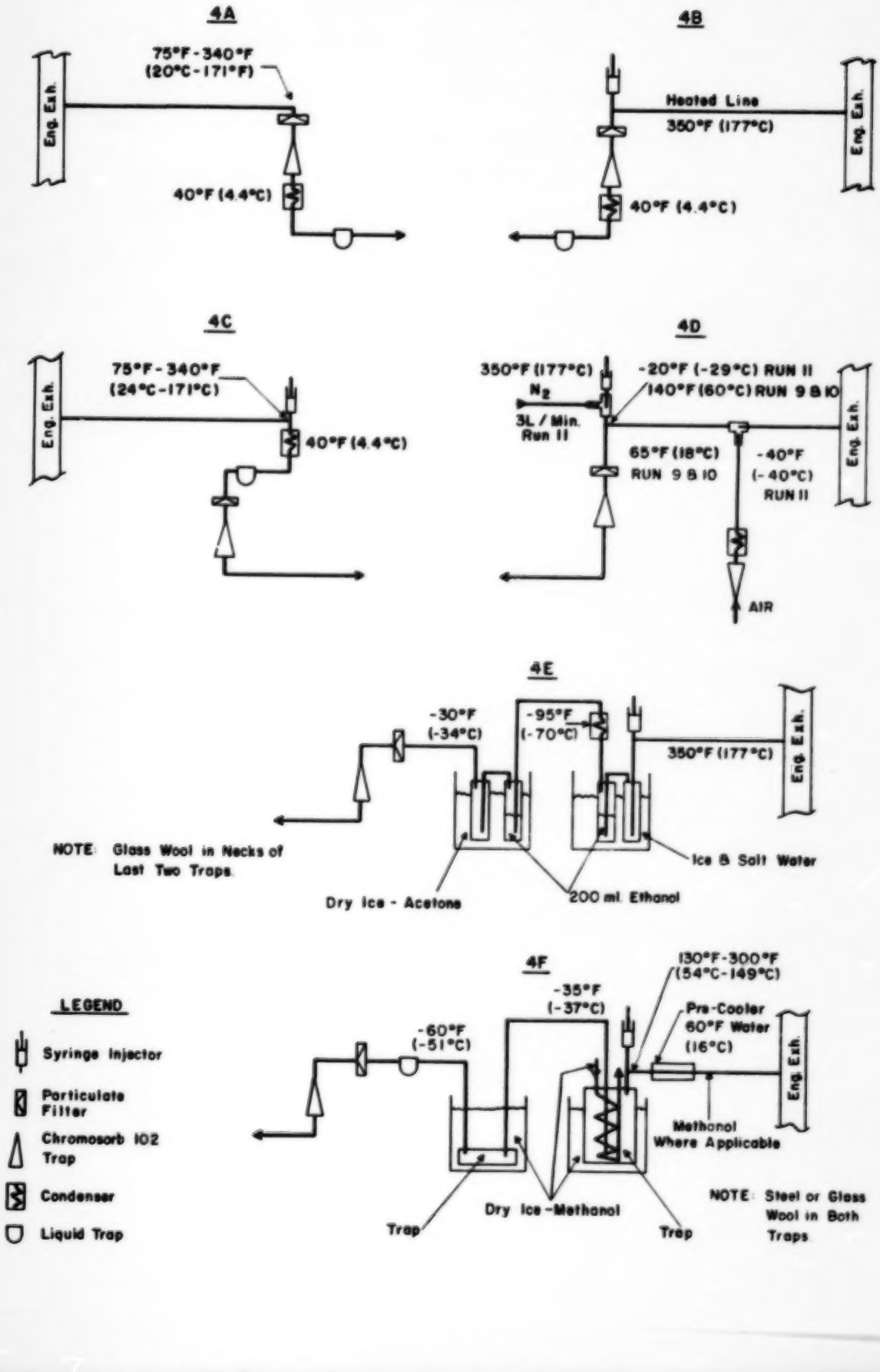
FIGURE 4
PNA COLLECTION SYSTEMS



Because BaP recovery was low with a heated sample line, it was decided that cooling the exhaust gas sample might be beneficial. Runs 6, 7, and 12 use a heat exchanger ahead of the filter (Figure 4-C) to lower the sample temperature. In Run 6, BeP loss was only 30% but BaP loss was 60%. In Run 7 the losses were 90% and 60% respectively, possibly because water was not used in the heat exchanger. In Run 12, (- 35%) of both BaP and BaA was recovered. By separate analyses in Run 12, approximately equal amounts of these compounds were found in the sampling lines, condenser and condensate, and on the filter. There was none of either compound on the Chromosorb-102 trap, suggesting that this trap is unnecessary for recovery of the PNA hydrocarbons. However, it is known that phenols do collect on this trap.

Since a water-cooled condenser did not significantly improve the total recovery, an air dilution system was tried (Figure 4-D). In these experiments (9, 10, and 11), instrument air, passed through a Chromosorb-102 trap to remove hydrocarbons, was introduced into the sampling system so that a 4/1 ratio of air to exhaust gas flow was maintained. These air dilution experiments were run at constant engine speed and load where it is easy to maintain steady flow. It would be possible to do the same thing for the 13-mode cycle but quite impractical to use air dilution with the smoke cycle and the proportional sampler.

In Run 9 an approximate 65% recovery of injected BeP was obtained, whereas in Run 10 the recovery of BaP was about 20%. Run 11, in which the added air was about -40°F (-40C), resulted in a sample stream temperature of -20F (-29°C). This run resulted in the best recovery of BaP, 30% of the amount injected. One problem encountered was the occasional freezing of the

exhaust stream as it mixed with the cold air. A solution to this problem was not found.

Calculating the recovery of injected PNA from these experiments is complicated by not knowing exactly how much was produced in the engine. Because we think the injected BaP greatly exceed the BaP from the engine, we have ignored the engine produced BaP in estimating PNA recovery.

B. Application of Radiotracers

The Project Group had been urging Gulf Research & Development Company to employ radioactive tracers to help understand what was happening during sampling. This approach had not been pursued because the analytical equipment was not available at Gulf Research & Development Company. In March 1974, representatives of the Ethyl Corporation and Chevron Research then volunteered to do the radioassays. Later, we arranged for New England Nuclear Company to do this analysis on a routine basis. Through the courtesy of Dr. Margaret Griffing of the Ethyl Corporation, the Contractor was supplied with a quantity of radioactive benzo(a)pyrene (C^{14}BaP). The C^{14}BaP permitted us to distinguish between BaP injected and BaP produced by the engine. The high purity of the C^{14}BaP was established by UV spectral analysis.

The use of C^{14}BaP in Experiment 11 showed several things. Both C^{14}BaP (6.42 µg) and BeP (3.97 ug) were injected while non-radioactive BaP (4.0 µg) and BeP (3.8 µg) were predeposited on the chromosorb trap. Upon analysis, 3.57 µg of BeP (~ 74%) was recovered from the lines and filter while 3.83 µg Bep (~ 100%) was recovered from the Chromosorb-102 trap. This recovery of BeP is considered excellent.

Table 3 gives an analysis of the C^{14}BaP distribution found in Experiment 11. Of the injected C^{14}BaP, 50% was recovered from the lines and filters, 2.2% in the BaP fraction from the chromosorb, and 21.5% in the form of degradation products from other parts of the system including the soot, the alumina column and other TLC fractions. The finding of 2% on the Chromosorb-102 means that very little BaP gets beyond the filter. The presence of only 3% C^{14}BaP in the BeP fraction is an indication of the very good separation of these compounds by the thin layer chromatographic procedure. Furthermore, these two compounds can be readily distinguished by UV spectroscopy.

Table 3 also contains the results of UV analysis for total BaP. These data (uncorrected for analytical losses) represent direct measurement of the compound using a calibration curve developed with BaP standard samples. The use of a radioactive tracer injected into the sample stream should permit measurement of the amount of BaP in the exhaust by applying a factor for recovery. This is not true when the radioactive spike is added to collected samples of exhaust emissions which contain a complex mixture of soot, unburned fuel, and partial oxidation products.

Even though the cold air dilution technique gave an adequate recovery of PNA, the difficulties due to water freezing in the line and of collecting a proportional sample, led us to look for another technique. We next tried a procedure recommended for use in analyzing stationary stack gas samples, Figure 4-E. This method utilizes a heated line followed by glass traps containing ethanol cooled in dry ice. The trapping went well but the method was unsatisfactory; only 10% of the injected BaP was recovered and only a trace of the BaA was found.

TABLE 3

ANALYSIS OF RADIOTRACER AND UV RESULTS
EXPERIMENT NO. 11

DDAD 3-53 Engine - 1800 rpm, 1/2 Load
6.42 µg C^{14}BaP Injected - 4.0 µg BaP Pre-Loaded on Chromosorb Trap

	Carbon^{14} Balance					
	C^{14}BaP		$C^{14}X$(3)		Total BaP by UV	
	µg	%	µg	%	µg	%
Lines & Filter	3.22	50.0	-	-	3.58(1)	N/A
Chromosorb Trap	0.14	2.2	-	-	1.62	37.0(2)
Other(3)			1.38	21.5		
Total	3.36	52.2	1.38	21.5	5.20	-

(1) Includes C^{14}BaP plus engine produced BaP.

(2) Corrected for C^{14}BaP found on trap.

(3) Other includes C^{14} activity measured in the following:

BeP fraction (0.097 µg), other TLC fractions (0.637 µg), soot (0.339 µg) and Alumina (0.305 µg). Most, if not all, of this activity is associated with degradation products of BaP. Weights reported are calculated as BaP based on radioassay.

Five other cryogenic trapping experiments were conducted using more efficient traps; a typical system is shown in Figure 4-F. In all these experiments, glass wool or steel wool was used in either the first or second trap to separate the condensed water. In Run 14, about 43% of BaP was recovered though only about 17% of BeP was recovered. Runs 15 and 16 were made without injecting PNA and represent direct comparisons with Runs 1 and 2. In Run 15 (as well as Run 14) methanol was injected to prevent ice formation. In Run 16, no methanol was used and water vapor was collected as snow on glass wool. In Run 21, methanol containing ammonia was injected to keep the condensate basic. In Runs 15 and 16, recoveries of PNA were lower than in Runs 1 and 2. Run 21 resulted in higher recoveries except for BghiP.

In all of the cryogenic experiments, difficulties were encountered because of the very large volumes of liquids that had to be extracted. Glass wool or steel wool had to be used to collect the entrained droplets of condensate. It was later found that recovery of PNA from either of these packing agents is difficult.

Two runs (18 and 19), were also similar to 1 and 2, except that a precooler in the sample line was used (Figure 5). This precooler is not intended to condense water vapor but to cool the exhaust to a temperature at which reactions are less likely to occur. Again, recoveries of PNA (except for BghiP) comparable to Runs 1 and 2 were obtained.

Table 4 lists the recovery of BaP and BeP produced by the engine on a constant exhaust volume basis. Experiments included in this table were conducted either without BaP injection or with the use of radioactive C^{14}BaP to distinguish from the engine produced material. The amount of engine produced

TABLE 4

ENGINE PRODUCED BaP

DDAD 3-53 Engine - Fuel 2-5

Test Conditions - 13-Mode Federal Cycle

Exp. No.	Collection System (Figure No.)	BaP ng/M^3*	BeP ng/M^3*
1	Direct filtration and Chromosorb-102 (4-A)	75	88
2	Direct filtration and Chromosorb-102 (4-A)	63	81
15	Cryogenic Bath, methanol injected, Direct filtration (4-F)	20	94
16	Cryogenic Bath, direct filtration (4-F)	47	28
17	Precooler, cryogenic trap, filter (4-F)	51	0
18	Precooler, direct filtration (5)	56	39
19	Precooler, direct filtration (5)	58	188
21	Precooler, cryogenic trap + filter + ammoniated methanol injected. (4-F)	100	90
	Average	58	76
	Std. Dev.	26	57

*Namograms per cubic meter of exhaust gas.

BaP is relatively constant. We suspect, based on these experiments, that engine produced PNA may have behaved differently than injected PNA. This hypothesis is fortified by measurements of injected PNA, Table 5. Data for this table were estimated either from C^{14}BaP injected or by subtracting the average engine produced PNA as estimated in Table 4. Only full 13-mode cycle runs were considered. Injected BaP recovery depended greatly on the sampling procedure and varied from 0 to 40%. One explanation for this difference is that the PNA from the engine were stabilized on the soot particles whereas the injected PNA reacted with constituents in the exhaust gases. Presumably, some of the injected PNA was destroyed.

If this is the case, then a collection system involving the precooler, filter, and chromosorb trap should be adequate to collect PNA from diesel exhaust.

With the Project Group's concurrence, the collection system shown in Figure 5 was adopted. It consists of a precooler to maintain sample temperature below 350°F (177°C), a 12" (30 cm) filter holder (Gelman Type A filters), the Chromosorb-102 trap and a heat exchanger with condensate trap. The 12" filter reduces the need to change filter papers during a run.

C. Analysis of Diesel Fuels

A principal aspect of the CAPE-24 Project was to determine typical PNA levels in diesel fuels. To this end, five ASTM 1-D and sixteen ASTM 2-D diesel fuels were obtained from around the country for analysis.

TABLE 5

RECOVERY OF INJECTED PNA

Exp. No.	System (Figure No.)	Percent Recovery BaP	BeP	BaA
3	Direct Filtration (4-B)	0		
4	Short exposure time of added PNA Direct Filtration (4-B)	41		
5	Short exposure time of added PNA Direct Filtration (4-B)		23	
6	40° Condenser (4-C)		35	
7	65° Air Cooled Condenser (4-C)		<7	
12	40° Condenser (4-C)	27		16
17	Precooler, Cryogenic Trap (4-F)	3*		
19	Precooler, Direct Filtration (5)	14*		
21	Precooler, -90° Cryogenic Trap (4-F)	17*		

*Radioactive Recovery.

FIGURE 5
FINALIZED PNA COLLECTION SYSTEM

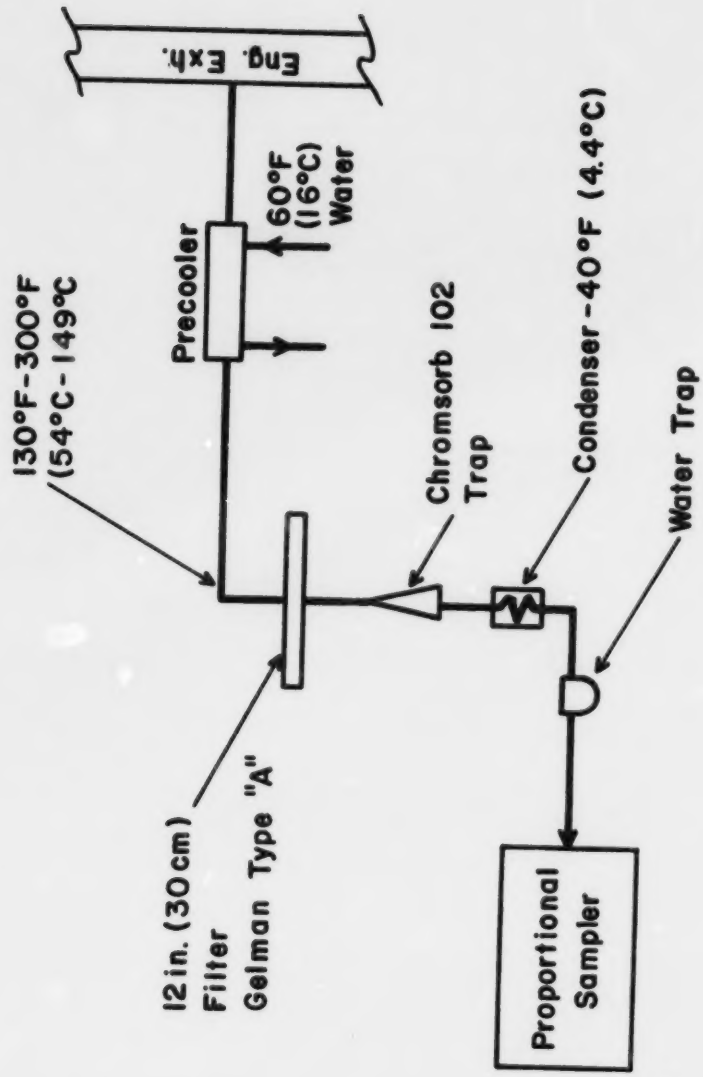


Table 6 gives the inspection data for these fuels as well as the cities where they were obtained. All fuels meet specifications set forth by engine makers.

Table 7 lists the analytical results for PNA. The first four columns are the principal PNA hydrocarbons that we have concentrated upon. Concentration of individual PNA ranges over nearly three orders of magnitude among the different fuels. There is no correlation of PNA content with either aromatic content or 90% distillation temperature.

A comparison of these results with gasoline is of interest. Gross[6] reports that gasolines vary in BaP content from "near zero" to an average 500 ppb to a field maximum 3000 ppb. The limited data in Table 6 suggests that ASTM 2-D fuels average less BaP, and probably other PNA, than gasoline even though the boiling range can encompass many PNA. This fuel difference may result from the fact that diesel fuels are essentially all non-cracked products obtained by distillation while gasolines are principally made from products that have been catalytically processed. Such processes may lead to either lighter components or to reformed components, both containing aromatics.

Fuel 2-5 was used in all of the preliminary engine studies. Since it is in the lowest range of PNA content, it is not desirable as the baseline fuel for the determination of representative PNA emissions. Because of the cost in both time and money of selecting a particular fuel with a given PNA content, it was decided to make a blend of eight fuels for the baseline studies. This fuel, 2-16, was prepared by blending eight

TABLE 6

SURVEY FUEL INSPECTION DATA

Code No.	Source	API Gravity	Density	Cetane Index	FIA		Sulfur	Distillation		
					Aromatics	Olefins		10	50	90
	No. 1 Fuels - Kerosene									
1-1	Philadelphia, PA	42.0	.8156	47	18.0	.5	0.015	380	420	464
1-2	Anacortes, WA	43.8	.8072	49	19.0	.5	0.007	360	412	476
1-3	Wood River, IL	44.0	.8063	51	18.5	1.0	0.032	373	418	477
1-4	Nederland TX	41.6	.8174	51	15.5	.5	0.044	402	447	492
1-5	Baton Rouge, LA	41.3	.8189	50	20.5	.5	0.039	381	440	498
	No. 2 Diesel Fuels									
2-1	Toledo, OH	34.2	0.8540	48	31.0	.5	0.21	434	516	599
2-2	Santa Fe Springs, CA	36.2	0.8438	52.5	28.5	.5	0.52	444	518	593
2-3	Port Arthur, TX	34.5	0.8524	46	28.5	.5	0.20	422	502	591
2-4	Cincinnati, OH	35.4	0.8478	45	30.5	.5	0.18	416	486	567
2-5	Philadelphia, PA	33.3	0.8588	42.5	39.0	.5	0.08	424	494	582
2-6	Jacksonville, FL	34.2	0.8540	47	26.5	0.5	0.13	418	518	610
2-7	Denver, CO	34.6	0.8520	44.5	33.5	2.0	0.32	400	490	586
2-8	Sullivan, MO	33.6	0.8572	42	37.5	.5	0.13	430	494	564
2-9	Waterville, ME	33.6	0.8572	41	22.0	.5	0.17	402	480	576
2-10	S. Gate, CA	34.0	0.8550	49	31.0	.5	0.28	443	530	606
2-11	Oklahoma City, OK	36.5	0.8422	50	27.5	.5	0.32	414	498	600
2-12	Portland, OR	36.6	0.8418	49	28.5	.5	0.21	408	488	578
2-13	Columbus, OH	35.7	0.8462	46	31.5	.5	0.20	408	486	564
2-14	Omaha, NE	35.6	0.8468	47	31.0	2.0	0.33	414	492	572
2-15	Wheeling, WV	35.0	0.8499	46	29.5	.5	0.14	431	496	560
2-16	Composite Test Fuel	36.9	0.8425	50	26.0	0.5	0.17	417	498	589
2-17	Columbus, IN	35.1	0.8493	48.5	35.1	4.0	0.21	412	508	596

TABLE 7

PNA CONTENT OF DIESEL FUELS µg/kg*

Compound: Code No.	BaP	BeP	BaA	BghiP	Chry	Tri	Pyr	Fluo	Anth	Phen	M-Anth	Total Phenols
					No. 1 Fuels - Kerosene							
1-1	3	3	3	3	ND	ND	160	90	40	ND	ND	4000
1-2	1	<1	<1	<1	ND	ND	ND	ND	ND	13	ND	3000
1-3	<1	<1	<1	<1	ND	ND	12	14	ND	54	ND	7000
1-4	<1	<1	<1	<1	ND	ND	21	7	1388	230	ND	12000
1-5	1	<1	<1	<1	ND	33	3	6	175	ND	ND	6000
					No. 2 Diesel Fuels							
2-1	69	177	132	28	452	3337	370	568	2868	ND	9300	22000
2-2	40	24	32	69	497	ND	ND	468	4261	ND	6620	34000
2-3	10	16	26	18	505	755	3037	3187	1016	ND	20700	23000
2-4	50	15	56	3	370	229	583	ND	6740	ND	15200	22000
2-5	9	10	15	9	808	1213	454	3644	2390	ND	20700	38000
2-6	274	52	422	172	105	585	315	3721	11800	ND	69800	19000
2-7	86	63	364	27	322	198	398	1454	19700	ND	43200	35000
2-8	256	263	81	205	92	ND	144	ND	37300	ND	22400	11000
2-9	9	3	87	2	76	81	268	875	4340	ND	28700	25000
2-10	2	<1	<1	<1	ND	ND	ND	ND	2000	ND	ND	19000
2-11	422	539	245	93	562	1432	1278	2489	9500	ND	17900	28000
2-12	12	10	466	7	264	905	1083	3125	13200	ND	60900	21000
2-13	<1	<1	<1	<1	ND	ND	88	119	3380	ND	3400	39000
2-14	312	261	374	83	1619	789	278	3465	57200	ND	37300	42000
2-15	10	<1	<1	<1	234	207	694	3000	9140	ND	31500	16000
2-16	41	75	108	26	72	35	144	869	31400	ND	19700	35000
2-17	11	35	142	18	595	595	367	1616	11100	ND	94400	74000
MDL	0.5	1	1	0.5	1	1.5	5	5	5	5	5	10

*Equal to parts per billion. ND = Not detected. MDL = Minimum detectable limit.

ASTM 2-D fuels available in the Pittsburgh area. Each supplier assured us that they had prepared the fuel and that it was not an exchange product. The suppliers were Amoco, Arco, Boron, Exxon, Mobil, Pennzoil, Sun, and Texaco. This blended fuel, which has typical inspection, has about six times the amount of the four PNA's of interest compared to Fuel 2-5 used in the preliminary experiments of this report. The PNA content is in the mid-range of the fuels surveyed.

D. Engine Repeatability Studies

Four 13-mode tests were conducted to measure repeatability of the total system. Engine operation was identical in each test. The baseline fuel (2-16) and the sampling apparatus shown in Figure 5 were used. Because injected BaP appeared to react differently than engine produced BaP that remained in the exhaust, the exhaust gas was not spiked with a C^{14} tracer. Instead, after the exhaust sample has been collected, the solutions from the soot extraction were spiked with C^{14}BaP to measure the BaP recovery during the analytical procedure.

Table 8 gives the results of these tests. Note first that the recovery of the C^{14}BaP spike is only about 28% compared with the 85% recovery when analyzing fuels (Table A-2). The 28% recovery of BaP indicates BaP and probably other PNA react with other exhaust products even in the liquid phase. The recovery of the three other principal PNA's are only corrected for analytical loss as described in Appendix A (Table A-2). No correction for recovery was applied to the remaining compounds because no recovery data have been obtained for them.

TABLE 8

13-MODE TEST REPEATABILITY

DDAD 3-53 Engine - Fuel 2-16

Experiment No.	22	23	24	26	Avg.	Std.Dev.
Percent Recovery of Radioactive BaP*	28.8	(28**)	20.0	28.2	26	4.2
Compound - µg per Test						
BaP, corrected	1.59	0.84	1.93	0.63	1.25	0.64
BeP	0.79	<.01	<.01	0.18	0.24	0.37
BaA	<.01	<.01	<.01	<.01		
BghiP	0.20	0.27	1.00	0.06	0.38	0.42
Chrysene	0.80	<.03	0.13	0.87	0.45	0.45
Pyrene	32.3	17.3	15.0	14.5	19.8	4.4
Phenanthrene	491	340	276	343	362.5	90
Fluoranthene	23.9	19.4	10.5	7.0	15.2	9.8
Phenanthrene Der.	443	300	675	464	471	154
Phenols	1280	840	752	504	849	306

* Radioactive spike added to solutions of sample before analytical recovery is started.

** The material recovered in this sample where BaP was expected did not contain BaP. From the UV spectra of another fraction, BaP was identified. A 28% recovery factor was assumed.

The amount of each individual compound in the exhaust sample shows a large variation. We have no explanation for this variation. The collected soot using the baseline fuel was far more tarry than the soot with Fuel 2-5. We also experienced greater difficulty in obtaining pure fractions during the separation because other UV-absorbing substances eluted with the PNA of interest. This may be an explanation of why the BaA yield is so much lower than BaP. In gasoline exhaust studies BaA always was found in larger amounts than BaP. Further work to improve the separation is planned.

E. Additional Engine Studies

At the request of the Project Group, a double length test (i.e., two 13-mode cycles) was conducted. The results appear in Table 9. This test should give an idea about sampling losses during sample collection.

Recovery of the C^{14}BaP spike was 28%, comparable to that obtained in the replicate tests. Because of the large amount of tar in this test, the filter paper containing the particulates was re-extracted and the solution separately spiked before processing. Not a great deal of additional PNA was recovered but the recovery for the C^{14}BaP spike was 87.5% which compares well with the 85% recovery for fuels. This result indicates that the species which react with PNA were extracted with the PNA in the first extraction.

It was also observed in the double length test that BaP, BghiP, pyrene, chrysene, and fluoranthene were recovered at about the same concentration as in the single length tests. This may indicate that these compounds are partially lost during sampling. Phenanthrene, the phenanthrene derivative and total phenols are recovered at about double the concentration.

TABLE 9

PNA RECOVERY IN DOUBLE LENGTH 13-MODE CYCLE TEST

	Average of 4 Single Length Tests	Std. Dev.	Double Length Test
Percent Recovery of Radioactive BaP	26	4.2	28.1(87.5)*
Compound	ug/Test	ug/Test	
BaP, Corrected	1.25	0.64	1.21
BeP	0.24	0.37	<.01
BaA	<.03	-	<.01
BghiP	0.38	0.42	0.78
Chrysene	0.45	0.45	1.00
Pyrene	19.8	4.4	25.9
Phenanthrene	362	90.	757
Fluoranthene	15.2	9.8	18.2
Phenanthrene Der.	431	154	1089
Phenols	849	306	1858

*Recovery of C^{14}BaP spike from second extraction of carbon deposits.

This suggests that the more stable compounds are recovered in better yield. However, because the test variability is so high, this experiment cannot be considered conclusive.

A single run has been made using the smoke cycle (see Appendix C). No difficulties were encountered in the use of the proportional sampler or the DATA-TRAK controller. The filter paper was found to be quite wet with condensed water, probably the result of the extensive idle in this cycle (even though the idle period was reduced from 5 minutes to only 1 minute). A very large amount of soot was collected in this test and the PNA found was low. Table 10 gives the PNA found for this test.

TABLE 10

PNA EMISSIONS FROM THE SMOKE CYCLE

Compound	ug/kg Fuel
BaP, Corrected	1.1
Pyrene	39.
Fluoranthene	17.
Phenanthrene	233.
Phenanthrene Derivative	320.
Phenol	2080.

No other PNA were found. In addition, recovery of the C^{14}BaP spike amounted to only 13.7%. Whether the low PNA yield indicates destruction after sampling or destruction due to the high exhaust temperature, is not yet known. The yield, particularly for the lower molecular weight species, are much lower in the smoke cycle test than in the 13-mode tests. These tests will be repeated.

F. Comparison of Exhaust PNA and Fuel PNA

Table 11 compares the recovery of PNA on the basis of ug per cubic meter of exhaust gases, ug per gallon, and ug per kg of fuel used. These data are average values for the four 13-mode cycles run with the baseline fuel. Also included in the table is the concentration of these PNA in the fuel. Anthracene was present in the fuel but not in the exhaust gas. Conversely, phenanthrene was in the exhaust gas but not in the fuel.

In spite of the fact that the first 21 runs were made with a variety of test procedures, a number of them can be used to calculate an average yield of PNA for Fuel 2-5. They include Runs 1, 2, 15, 16, 17, 18, 19, and 21 for which analytical data were available. Table 12 compares the PNA recovery in ug/test for both Fuel 2-5 and 2-16. It is not possible to give a corrected recovery for BaP with Fuel 2-5 since radioactive BaP, if incorporated, was injected into the exhaust sample stream. The PNA in the exhaust gas from both fuels is similar but with differences. The variability based on standard deviations is comparable. There is no evidence that variation in sampling procedure used with Fuel 2-5 has increased the variability of recovery. The low yield of BaA with Fuel 2-16 may be an artifact due to the separation procedure. With this fuel, a considerable amount of background material present with the expected BaA cut.

TABLE 11

AVERAGE PNA EMISSIONS FROM FOUR 13-MODE CYCLES

DDAD 3-53 Engine - Fuel 2-16

Compound	$\mu g/M^3$ Exhaust Gas	µg/Gal. Fuel Burned	µg,Kg. Fuel Burned	µg/Kg. In Fuel
BaP	0.158	22	6.9	41
BeP	0.031	4	1.3	75
BaA	-	-	-	108
BghiP	0.048	7	2.2	26
Chrysene	0.035	5	1.6	72
Pyrene	2.501	349	110	144
Anthracene	-	-	-	31400
Fluoranthene	1.88	253	79	869
Phenanthrene	46.1	6410	2013	-
Phenanthrene Der.	59.8	8280	2600	-
Phenols	107.2	14900	4680	35000

TABLE 12

COMPARISON OF PNA FOUND WITH FUELS 2-5 AND 2-16

	Fuel-2-5		Fuel 2-16	
	Average ug/Test	Std. Dev.	Average ug/Test	Std. Dev.
BaP	0.48	0.24	1.25*	0.64
BeP	0.58	0.44	0.24	-
BaA	0.50	0.57	< 0.01	-
BghiP	1.14	1.5	0.38	0.42
Chry	1.48	0.77	0.45	0.45
Pyr	21.9	8.2	19.8	4.4
Phen	448.	256.	362.	90.
Fluo	ND	ND	15.2	9.8
Phen Der.	ND	ND	431.	154.
Phenols	1014.	266.	849.	306.

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*Corrected for analytical loss using C^{14} spike.

The unburned fuel per test is calculated to be 0.102 kg, from Table B-1. From the measured fuel consumption (16.51 kg), the fraction unburned fuel in the exhaust is 0.62%. This unburned fuel contains, in addition to the original fuel, a variety of thermal degradation products. If synthesized PNA were not present in these degradation products, the maximum yield of PNA would be 0.62% of the PNA in the fuel consumed, assuming all fuel components burn equally well.

Table 13 compares the PNA found in the exhaust in ug/kg of fuel burned and the percent PNA of the original fuel for Fuels 2-5 and 2-16. Because the data on BaP for Fuel 2-16 has been corrected to account for losses, it is probable that the yield of this compound is essentially the same for both fuels. In nearly every case, except anthracene, the percent of compound present is much greater than 0.62% of the material in the original fuel. This in turn supports the theory that PNA are formed as byproducts of incomplete combustion.

G. Comparison of Gasoline and Diesel PNA emissions

While it is of interest to compare PNA emissions from gasoline and diesel engines it must be remembered that the engine tests are conducted using completely different procedures. Data reported in Table 14 for the gasoline engine were obtained while the vehicle was operated repetitively in the original 7-mode Federal cycle.[6] Data for the diesel engine were obtained from the 13-mode Federal diesel emission procedure. Further, the sampling and analytical procedures used in the two studies are totally different. Ignoring these differences, Table 14 suggests that the diesel engine produces less PNA than the uncontrolled gasoline engine in terms of emissions per gallon of fuel burned.

TABLE 13

COMPARISON OF EXHAUST PNA TO PNA IN FUEL

	Fuel 2-5		Fuel 2-16	
	µg/kg Fuel Burned	% of Fuel PNA in Exhaust	µg/kg Fuel Burned	% of Fuel PNA in Exhaust
BaP	2.7	30	7	17
BeP	3.3	32	1	2
BaA	2.7	18	-	0
BghiP	6.5	72	2	8
Pyr	121	27	110	76
Chry	8.2	1	3	4
Anth	0	0	0	0
Flou	0	0	85	10
Phen	2409	∞	2015	∞
Phen Der.	-	-	2396	∞
Phenols	5600	15	4723	13

TABLE 14

PNA EMISSIONS FROM DIESEL AND GASOLINE ENGINES

ug/gal. of Fuel Burned

	Uncontrolled Car	Controlled Car	DDAD-3-53 Engine
Fuel BaP (µg/gal)	45	185	132
BaP	77	13	22
BeP	244	48	4
BaA	119	32	-
BghiP	358	56	7
Chry	231	87	7
Pyr	2228	411	349
Fluo	1869	383	269

H. Analysis of Gaseous Emissions

Part of the requirement for this project is to determine gaseous emissions during the 13-mode cycle, and smoke emissions during the smoke cycle. Results are in Table 15. Analytical data for each mode is given in Appendix C. These data were obtained from the four reproducibility tests plus the one smoke cycle using the baseline fuel.

Both gaseous and smoke emissions were below 1974 standards for heavy duty diesel engines and are typical for this engine model.

TABLE 15

GASEOUS ENGINE EMISSIONS

Engine DDAD-3-53 - - Fuel 2-16

	13-Mode Cycle g/BHP-Hr.
CO	8.8
HC + NO_x	10.9
HC	1.5
NO_x	9.4
NO	7.5

Mode	Smoke Cycle % Opacity
Acceleration	18
Lugging	14
Peak	35

V. CONCLUSIONS

1. An adequate sampling system has been developed for PNA collection. It consists of a gas precooler, particulate filter and a Chromosorb-102 trap.

2. Recovery of PNA from diesel exhaust may be reduced by reactions of PNA with other constituents in the exhaust. Injected PNA shows greater variability in recovery with different sampling systems than does the remaining engine emitted PNA.

3. Twenty diesel fuels ranged widely in PNA content, from 1 ppb to 422 ppb for BaP and to 466 for BaA. These concentrations are low relative to gasolines which have been found to contain up to 3100 ppb of BaP.

4. There appears to be little effect due to fuels in yield of PNA from the DDAD-3-53 engine.

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APPENDIX A

ANALYTICAL PROCEDURES

I. PNA HYDROCARBONS IN DIESEL FUEL

The polynuclear aromatics (PNA) were concentrated by alumina gel column chromotography, separated by thin layer chromotography, and identified by ultraviolet spectrophotometry.

All solvents, reagents, and equipment were free of PNA and PNA separations were performed in subdued light to reduce degradation of PNA.

A. PNA Concentration

The analytical scheme used to separate the PNA hydrocarbons from the diesel fuel is given in Figure A-1. The concentration step is done with a 35 x 1.9 cm glass column packed with 60 g of 2.5% water deactivated Woelm Alumina. In practice, 20 grams of fuel is placed on the column and eluted with a group of solvents. The first 400 ml of isooctane (IO) and the 300 ml of IO containing 20% benzene removes most of the saturates and light aromatics. Cut 3 was eluted with 800 ml of a 50/50 mixture of IO and benzene followed by 100 ml of benzene. Cut 4, not used in this work, is obtained by an additional 700 ml of benzene. The four PNA analyzed for in this investigation, benz(a)anthracene (BaA), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), and benzo(g,h,i)perylene (BghiP) are recovered quantitatively as shown in Table A-1.

The water content of the alumina gel is important. The water content of the gel was determined by the weight loss of 10 g of gel after

FIGURE A-1

DIESEL FUEL PNA SEPARATION PROCEDURE

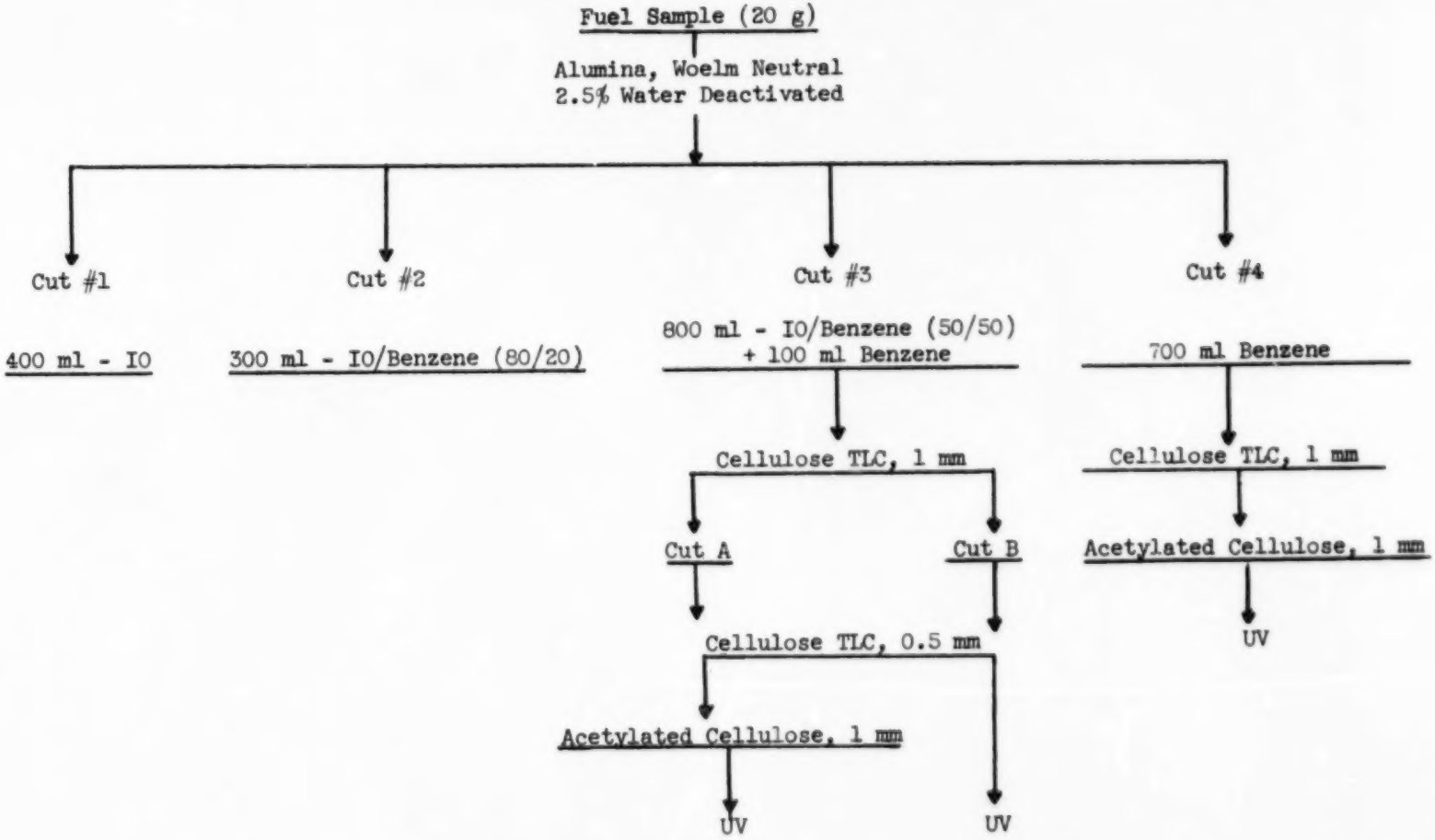


TABLE A-1

PNA RECOVERY - ALUMINA, NEUTRAL, 2.5% WATER DEACTIVATED

10 µg Each PNA in Isooctane

Cut	Ml.	Eluant	Pyrene µg	Pyrene %	BaA µg	BaA %	BeP µg	BeP %	BaP µg	BaP %	BghiP µg	BghiP %
1	400	I-0										
2	300	I-0/Benz.(80/20)										
3-1	50	I-0/Benz.(50/50)	4.0	40								
3-2	50	"	4.1	41								
3-3	50	"	1.9	19								
3-4	50	"										
3-5	50	"			1.2	12						
3-6	50	"			2.6	26						
3-7	50	"			2.4	24	2.2	22				
3-8	50	"			2.0	20	3.7	37				
3-9	50	"			1.0	10	2.8	28				
3-10	40	"					1.3	13	1.4	14		
3-11	50	"							2.1	21		
3-12	50	"							1.9	19		
3-13	50	"							2.0	20		
3-14	50	"							2.6	26		
3-15	50	"									2.7	27
3-16	50	"									2.6	26
4-1	50	Benzene									2.8	28
4-2	50	Benzene									1.9	19
		TOTAL	10.0	100	9.2	92	10.0	100	10.0	100	10.0	100

heating for 10 minutes at a red heat over a Bunsen burner. Then the desired amount of unheated gel is placed in a bottle and the necessary amount of water added to give the desired water content. After equilibration overnight, the content is verified by repeating the above procedure. The water content should be ±0.1 wt. % of the desired level.

B. Thin Layer Separation

The cellulose and acetylated cellulose must be prewashed to remove interfering ultraviolet absorbing material. A slurry of the absorbent in methanol is agitated in a Waring blender for 5 minutes, transferred to a Buchner funnel and rinsed twice with more methanol before air drying.

The cellulose thin-layer plates are prepared by adding 26 g of cellulose to 170 ml water and mixing for 3 minutes in a Waring blender. The solution is transferred immediately to the applicator for the preparation of about 4 plates 20 x 20 cm and 1 mm thickness. After air drying, the plates are developed with I0 to remove additional interfering components, then stored in a dessicator.

The acetylated cellulose plates are prepared by mixing 40 g of acetylated cellulose and 150 ml of 95% ethanol in a Waring blender for 3 minutes. This provides sufficient material for about 8 plates 20 x 10 cm x 1 mm. These plates are air dried and stored in a dessicator.

C. Cellulose "Prep" Plate

The effluent of interest, for instance cut 3, is concentrated to approximately 0.3 ml in benzene and streaked in a very narrow band with a 50 µl syringe about 2 cm from the bottom and 2 cm from the sides of the

plate. Also, a spot of BaP is placed on the extreme side of the plate as a reference compound. The plate is then immersed, from the end opposite the sample, in a solution of 20% N,N-dimethylformamide (DMF) in ether, which migrates to within 0.5 cm of the applied sample. The plate is removed and air dried for approximately 15 seconds, then developed in the reverse direction with IO as the mobile phase.

Two cuts, A and B are removed from the cellulose "prep" plate for further separation. This "prep" step is usually necessary because of the relatively high concentration of lower molecular weight PNA making the detection of individual bands difficult. The plate is observed under ultraviolet light and the upper limit of Cut A marked with a pencil line between the R_f for BaP, as observed with the BaP standard, and the next higher R_f band, which is pyrene. The lower limit of Cut A extends down to, but not including, the starting line. Cut B is the material remaining on the plate excluding the uppermost, usually yellow, band which is discarded. These cuts are scraped from the plate into separate Pyrex brand extraction thimbles with a coarse porosity disc and Soxhlet extracted for 2 hours with benzene.

D. Cellulose Separation

Cut A is concentrated to about 0.3 ml benzene, whereas Cut B, due to higher solute concentrations, is diluted to 25 ml with benzene and then an aliquot, usually 1 ml, concentrated to 0.3 ml. These samples are applied to cellulose plates 0.5 mm thick along with a BaP standard at the side and developed as done previously for the cellulose "prep" plates. The plates are then examined briefly under ultraviolet light and the fluorescent bands observed, outlined with a pencil and the R_f compared to the BaP standard.

Appendix A

The outlined bands are transferred into separate 50 ml beakers and extracted three times with about 10 ml of hot methanol. The methanol is filtered through a pressure sintered glass filter into a 50 ml Erlenmeyer flask and concentrated to approximately 0.3 ml of benzene by adding 30 ml of benzene in 10 ml increments.

This concentrate is then applied to 20 x 10 cm cellulose acetate plates 1 mm thick and developed by a mobile phase consisting of ethanol, toluene and water (13:4:4, v/v/v). When the solvent migrates to within 1 cm of the top, the plate is removed and the fluorescent bands outlined and transferred directly into the pressure filter and washed with hot methanol in three 10 ml increments. The filter effluent is collected in 50 ml Erlenmeyer flasks and, after adding 1 ml n-hexadecane, evaporated to 1 ml. Three 10 ml portions of IO are added to the flasks with evaporation after each addition to remove all other solvents. The 1 ml n-hexadecane is transferred to a 1 cm ultraviolet cell and scanned for absorption in the 220-400 nm region. Identification and quantification is done by reference to previously prepared absorption spectra.

E. Recovery

Two experiments were done to study the recovery and repeatability of the procedure for the fuel analysis system. In each case, 1 ug each of BaA, BaP, BeP, and BghiP were added to 20 g of a No. 2 fuel oil. This fuel blend was then put through the complete analytical separation. The result, given in Table A-2, indicates the average recovery and repeatability of the procedure after correction for the 10 µg/kg max., PNA in the original oil. The average recovery data have been used to correct the fuel survey results.

TABLE A-2

PNA RECOVERY STUDY, NO. 2 FUEL OIL

PNA Added	Amount	% Recovery	Avg. % Recovery
Benz(a)anthracene	1 µg	72, 74	73
Benzo(a)pyrene	1 µg	81, 88	85
Benzo(e)pyrene	1 µg	100, 100	100
Benzo(g,h,i)perylene	1 µg	98, 94	96

Appendix A

II. DIESEL EXHAUST GAS ANALYSIS

The exhaust gas sample preparation steps are shown in Figure A-2. Each of the elements of the exhaust gas sampling system are considered separately because of the various procedures used.

A. Chromosorb-102

The Chromosorb-102 is reverse flushed with 100 ml of methanol followed by 100 ml of benzene which removes phenolic and hydrocarbon materials. Quite often this trap contains some moisture and the pre-wash with methanol allows a more effective subsequent wash with benzene.

B. Lines

All of the connecting lines in the exhaust sampling system are disassembled and cleaned thoroughly with a brush and benzene.

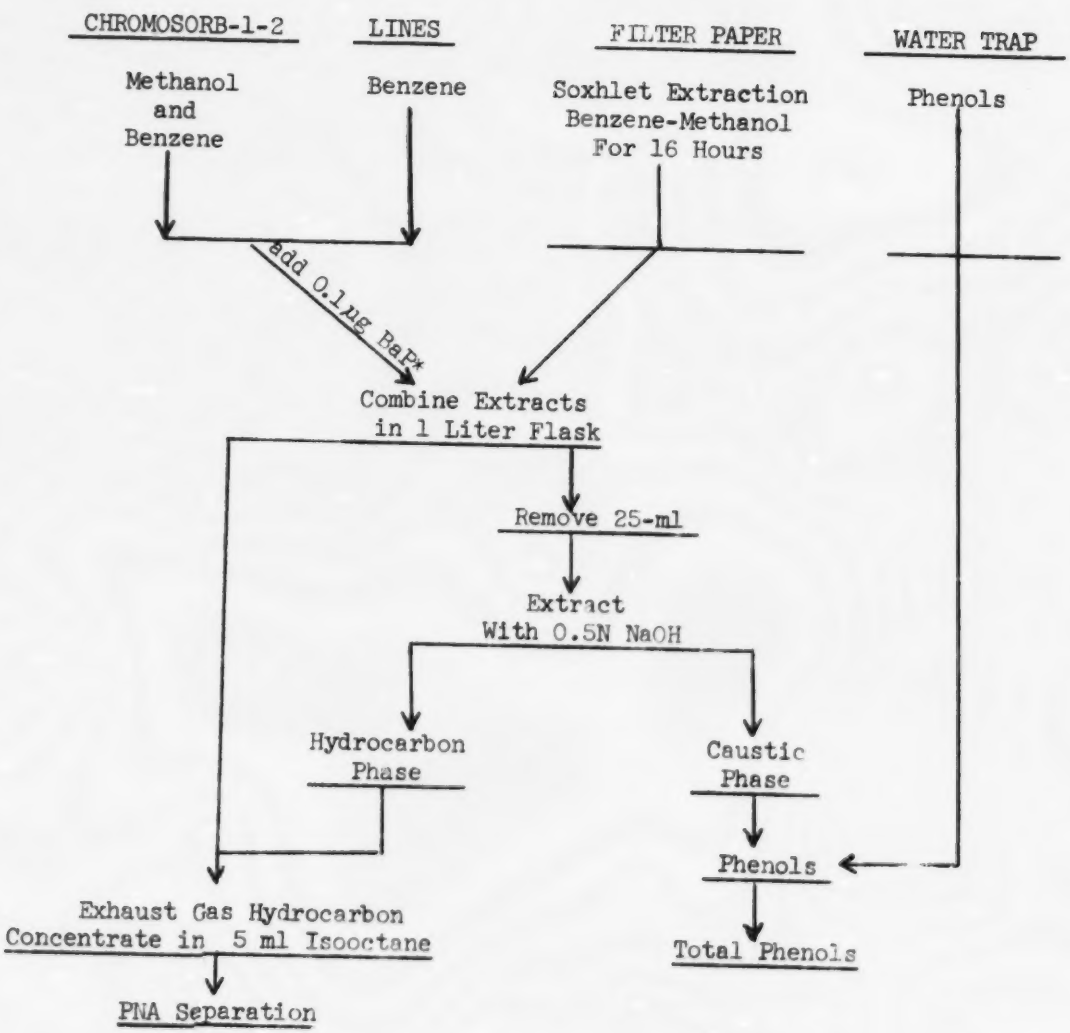
C. Filter Paper

The filter housing is cleaned with a brush and benzene and the solvent added to that obtained when the lines were washed. The filter paper is cut into about 1 cm squares and placed in an extraction thimble. Then the solutions from the Chromosorb-102 trap, lines and filter housing are filtered through the extraction thimble into a 1-liter volumetric flask and approximately 0.1 μg C^{14}BaP added. Thus, any soot particles in the rinse solutions, are retained in the thimble along with the filter paper. The filter paper and soot are extracted for 16 hours with a benzene-methanol mixture (60-40, v/v).

The Soxhlet extract is added to the 1-liter flask and the contents adjusted to the mark with isooctane. Then, 25 ml is withdrawn from the flask, diluted with 100 ml isooctane and caustic extracted three times with 0.5 N

FIGURE A-2

EXHAUST GAS SAMPLE PREPARATION



sodium hydroxide. The caustic phase is added to the contents of the water trap and analyzed for total phenol. The extracted hydrocarbon phase is recombined with the contents of the 1-liter flask and evaporated on a steam bath under a stream of nitrogen to approximately 5 ml of isooctane.

D. PNA Concentration

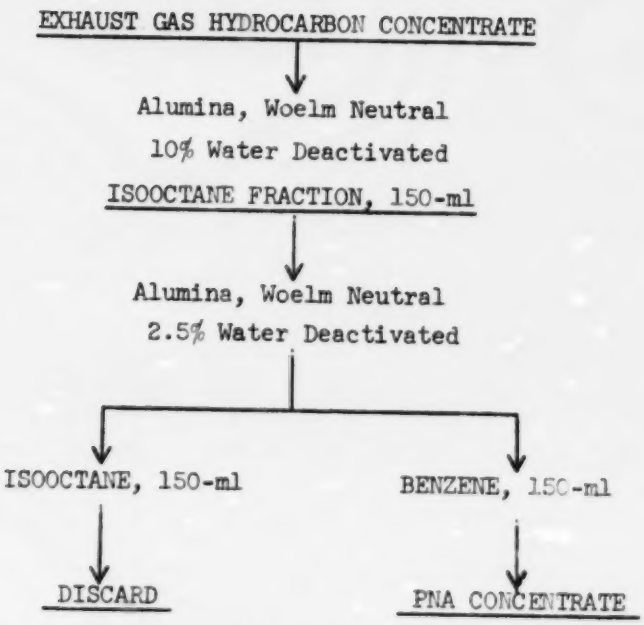
The PNA concentration scheme for exhaust gas is shown in Figure A-3 which removes interfering ultraviolet absorbing material and unwanted saturate and aromatic components.

The hydrocarbon concentrate in about 5 ml isooctane, obtained by the exhaust gas sample preparation, Figure A-2, is placed on a 20 x 1.7 cm glass column containing 15 g of alumina, Woelm neutral, deactivated with 10% water, and eluted with 150 ml isooctane. The isooctane eluate is allowed to flow directly onto a second column of the same dimensions, but containing 15 g of alumina, Woelm neutral, deactivated with 2.5% water. After the top column is dry and the bottom column still has a layer of isooctane over the alumina, the bottom column is separated and eluted with 150 ml of benzene. This fraction, which contains the PNA of interest, is concentrated to about 0.3 ml in benzene and separated by cellulose and acetylated cellulose TLC as shown in Figure A-1 and described in the fuel oil analysis section.

This two-column separation was verified by separating a known mixture of PNA in isooctane. Recoveries ranged between 90 and 100% for benzo(a)pyrene, benzo(g,h,i)perylene and coronene. All PNA of interest for this investigation lie between the elution volumes of these compounds.

FIGURE A-3

EXHAUST GAS SAMPLE PNA SEPARATION



Appendix A

III. PHENOL ANALYSIS

A short study was undertaken to develop a method for phenol determination in diesel fuels and exhaust gas systems.

Two methods were investigated. A solvent extraction gas chromatographic method to determine individual phenols and a solvent extraction colorimetric method using 4-aminoantipyrene for total phenols.

Total phenol, after extraction with sodium hydroxide, is detected rapidly and accurately down to 10 parts per billion by the colorimetric method. Individual phenols by the extraction gas chromatographic method are detected down to one part per million for phenol, cresols and xylenols and five parts per million for tri and tetramethyl phenols. However, the higher molecular weight phenols also present in diesel exhaust do not elute from the gas chromatographic column. Therefore, we elected to use the total phenol procedure.

A. Preparation of Phenol Concentrate by Caustic Extraction

For this program it is assumed that all phenols of interest are extractable by aqueous sodium hydroxide. This would include many alkyl substituted phenols, naphthols, indanols, and possibly higher number of ring phenols.

A weighed sample (165 g) of diesel fuel or kerosene is extracted three times with 0.5 N sodium hydroxide (25 ml each). In the case of exhaust gases, a PNA solution is obtained by solvent washing all sample lines and traps, solvent extracting the aqueous condensate, and the soot and diluting the combined solutions to one liter. An aliquot (25 ml) of this solution is then extracted with three 25 ml portions of 1.0 N sodium hydroxide. The alkali extracts are combined and diluted to a known volume.

Appendix A

B. Total Phenol Analysis

The 4-aminoantipyrine method for total phenol was investigated. In this procedure phenols in an aqueous solution react with 4-aminoantipyrine at a pH of 10 $\pm$0.2 in the presence of potassium ferricyanide to form a colored antipyrine dye. This dye is extracted from the aqueous solution with chloroform and its percent transmission read at 460 nm. The concentration of the phenolic compounds is calculated as total phenol (C_6H_5OH).

1. Color Development

The caustic washings are adjusted to a pH of 10 with phosphoric acid, and diluted to 300 milliliters with water. Phenol I and II pillows* containing various reagents needed for pH control and color development are added to an aliquot of the solution further diluted to 300 ml. The colored dye formed at room temperature is then extracted after two minutes with 30 milliliters of chloroform into a one-inch test tube. Percent transmission at a wave length of 460 nm is measured by means of a Bausch & Lomb Spectronic 20 and compared with a previously prepared calibration chart to give the total micrograms phenol present in the 300 milliliter sample taken for color development.

2. Calculations

For diesel fuel, heating oil, kerosene:

$$\underset{\text{(total phenol)}}{\text{ppm}} = \frac{\text{micrograms phenol from calibration chart}}{\text{weight of sample in grams}}$$

For exhaust gas:

$$\underset{\text{(total phenol)}}{\text{Micrograms}} = \left(\frac{\text{Original sample vol.}}{\text{aliquot}}\right) \text{X Micrograms from calib. chart}$$

*Obtained from the Hach Chemical Company, Ames, Iowa.

Appendix A

3. Application of Total Colorimetric Phenol Method

This colorimetric method was evaluated for various fuels. The results are given in Table A-3. Each fuel was analyzed three times and as can be seen, good agreement was obtained. Different sample weights of each fuel were taken to insure that the phenols were quantitavely extracted by the caustic.

C. Chromatographic Analysis

The combined caustic extracts are acidified and the phenols extracted by three ethyl ether washings (about 40 ml each). Organic acids are removed from the combined ether extracts with a small volume (about 10 ml) of saturated sodium bicarbonate solution. Finally, dissolved water is removed from the ether by passing it through a glass column containing anhydrous sodium sulfate.

The ether is evaporated, under nitrogen, on a steam bath to a volume less than one milliliter. Orthochlorophenol (0.2 mg) was added for use as an internal standard. An aliquot of this volume is injected into a gas chromatograph equipped with a capillary column.

Figure A-4 shows a chromatogram of the phenols in an engine exhaust.

Table A-4 shows the gas chromatograph operating conditions and Table A-5 shows approximate retention times and flame sensitivity of various phenols.

D. Methods Comparison

The total phenol (4-aminoantipyrene) and gas chromatographic procedures are compared in Table A-3. The GC Method detects considerably less total phenol than the 4-aminoantipyrene procedure. The likely

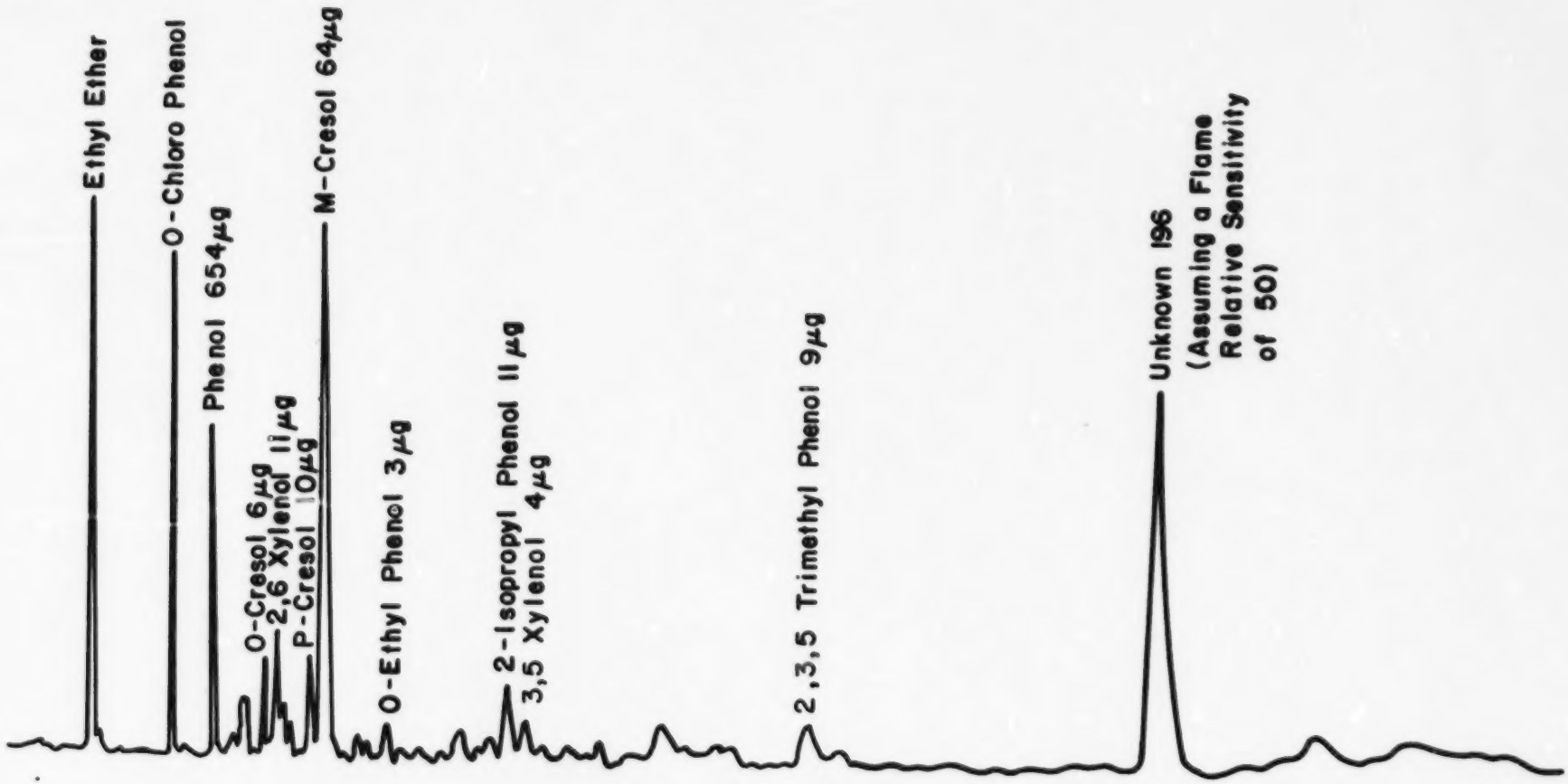


FIGURE A-4
GAS CHROMATOGRAPH OF PHENOLS IN DIESEL EXHAUST

TABLE A-3

TOTAL PHENOLS

4-Aminoantipyrene

Sample Size Grams		Total Micrograms Phenol	ppm
1.5147	#2 Heating Oil	35	23
1.3052		29	22.2
2.0830		46	22.1
1.0793	Diesel Fuel	30	27.8
1.1156		30	26.9
1.5058		40	26.6
1.0554	Kerosene	3	2.8
1.3023		5	3.8
1.7927		7	3.9

GC ANALYSIS

#2 Heating Oil	7
Diesel Fuel	19

TABLE A-4

GAS CHROMATOGRAPHIC OPERATING
CONDITIONS FOR PHENOL ANALYSIS

Instrument	Perkin Elmer 900
Column	150' x .02" I.D. capillary
Substrate	Didecylphthalate + 10% H_3PO_4
Carrier Gas	Helium, 12#/square inch
Hydrogen Flow	PSI
Air Flow	PSI
Column Temperature	130°C Isothermal
Detector	Flame Ionization
Injector Temperature	250°C
Detector Temperature	250°C
Splitter Ratio	1:90
Sample Size	6 µl
Attenuation	As needed

TABLE A-5

GAS CHROMATOGRAPHIC
SEPARATION OF PHENOLS

Component	Approx. minutes past injection	Flame Sensitivity(a)
o-Chlorophenol	4	0.45
Phenol	6	0.61
o-Cresol	7.5	0.66
2,6-Xylenol	7.7	0.68
p-Cresol	9	0.60
m-Cresol	9.5	0.60
o-Ethyl phenol	10.5	0.63
2,4-Xylenol	10.8	0.60
2,5-Xylenol	10.9	0.68
2,3-Xylenol	12.0	0.62
p-Ethyl phenol	12.9	0.60
iso-Propylphenol	13.0	0.70
3,5-Xylenol	13.4	0.69
3,4-Xylenol	16.0	0.61
2,3,5-Trimethylphenol	22.0	0.60
2,3,4,6-Tetra-methylphenol	25.0	0.47

(a) W. A. Dietz, J. Chromatog. Sci., 10, 423 (1972).

explanation for this discrepancy is that the phenols in diesel fuels and exhaust gases contain naphthols and other polynuclear phenols in addition to alkyl phenol derivatives. These higher ring phenols do not readily elute from the GC column. For example, 1-naphthol had not eluted from the column by 60 minutes, whereas tetramethylphenol elutes in only 25 minutes.

On the basis of this limited study, and the fact that the total phenol method takes considerably less time, it was decided to use the total phenol 4-aminoantipyrene procedure for this program.

APPENDIX B

DIESEL ENGINE OPERATING PROCEDURES

The test procedures used for diesel engine operation are published in the Federal Register, Volume 37, pages 24297 and 24310-24311, November 15, 1972. The description of the test procedure and dynamometer operation are reproduced below for each procedure:

1. Emissions Cycle - 13-Mode or Gaseous

§ 85.974-9 Test procedures.

The test procedures described in this and subsequent sections will be the test program to determine the conformity of engines with the standards set forth in § 85.974-1.

(a) The test procedure begins with a warm engine and consists of a prescribed sequence of engine operating conditions on an engine dynamometer with continuous examination of the exhaust gases.

(b) The test is designed to determine the brake-specific emissions of hydrocarbons, carbon monoxide and oxides of nitrogen when an engine is operated through a cycle which consists of three idle modes and five power modes at each of two speeds which span the typical operating range of diesel engines. The procedure requires the determination of the concentration of each pollutant, the exhaust flow and the power output during each mode. The measured values are weighted and used to calculate the grams of each pollutant emitted per brake-horsepower hour.

(c) When an engine is tested for exhaust emissions or is operated for durability testing on an engine dynamometer, the complete engine shall be tested with all standard accessories which might reasonably be expected to influence emissions to the atmosphere installed and functioning.

§ 85.974-11 Dynamometer procedure.

(a) The following 13 mode cycle shall be followed in dynamometer operation tests of heavy-duty diesel engines:

Mode No.	Engine speed	Percent load
1	Low idle	0
2	Intermediate	2
3	do	25
4	do	50
5	do	75
6	do	100
7	Low idle	0
8	Rated	100
9	do	75
10	do	50
11	do	25
12	do	2
13	Low idle	0

(b) During each mode the specified speed shall be held to within 50 r.p.m. and the specified torque shall be held to within 2 percent of the maximum torque at the test speed. For example, the torque for mode 4 shall be between 48 and 52 percent of the maximum torque measured at the intermediate speed.

Appendix B

2. Smoke Cycle

§ 85.874–9 Test procedures.

The procedures described in this and subsequent sections will be the test program to determine the conformity of engines with the standard set forth in § 85.874–1.

(a) The test consists of a prescribed sequence of engine operating conditions on an engine dynamometer with continuous examination of the exhaust gases. The test is applicable equally to controlled engines equipped with means for preventing, controlling, or eliminating smoke emissions and to uncontrolled engines.

(b) The test is designed to determine the opacity of smoke in exhaust emissions during those engine operating conditions which tend to promote smoke from diesel-powered vehicles.

(c) The test procedure begins with a warm engine which is then run through preloading and preconditioning operations. After an idling period, the engine is operated through acceleration and lugging modes during which smoke emission measurements are made to compare with the standards. The engine is then returned to the idle condition and the acceleration and lugging modes are repeated. Three sequences of acceleration and lugging constitute the full set of operating conditions for smoke emission measurement.

(d) All emission control systems installed on or incorporated in a new motor vehicle engine shall be functioning during all test procedures in this subpart.

§ 85.874–11 Dynamometer operation cycle for smoke emission tests.

(a) The following sequence of operations shall be performed during engine dynamometer testing of smoke emissions, starting with the dynamometer preloading determined and the engine preconditioned (§ 85.874–16(c)).

(1) *Idle mode.* The engine is caused to idle for 5 to 5.5 minutes at the manufacturer's recommended low idle speed. The dynamometer controls shall be set to provide minimum load by turning the load switch to the "off" position or by adjusting the controls to the minimum load position.

(2) *Acceleration mode.* (i) The engine speed shall be increased to 200±50 r.p.m. above the manufacturer's recommended low idle speed within 3 seconds.

(ii) The engine shall be accelerated at full-throttle against the inertia of the engine and dynamometer or alternately against a preselected dynamometer load such that the engine speed reaches 85 to 90 percent of rated speed in 5±1.5 seconds. This acceleration shall be linear within ±100 r.p.m.

(iii) When the engine reaches the speed required in subdivision (ii) of this subparagraph, the throttle shall be moved rapidly to the closed position and the preselected load required to perform the acceleration in subdivision (iv) of this subparagraph shall be applied. The engine speed shall be reduced to the speed of maximum rated torque or 60 percent of rated speed (whichever is higher), within ±50 r.p.m. Smoke emissions during this transitional mode are not used in determining smoke emissions to compare with the standard.

(iv) The throttle shall be moved rapidly to the full-throttle position and the engine accelerated against the preselected dynamometer load such that the engine speed reaches 95 to 100 percent of rated speed in 10±2 seconds.

(3) *Lugging mode.* (i) Proceeding from the acceleration mode, the dynamometer controls shall be adjusted to permit the engine to develop maximum horsepower at rated speed. Smoke emissions during this transitional mode are not used in determining smoke emissions to compare with the standard.

(ii) Without changing the throttle position, the dynamometer controls shall be adjusted gradually to slow the engine to the speed of maximum torque or to 60 percent of rated speed, whichever is higher. This engine lugging operation shall be performed smoothly over a period of 35±5 seconds. The rate of slowing of the engine shall be linear, within ±100 r.p.m.

(4) *Engine unloading.* After completion of the lugging mode in subparagraph (3)(ii) of this paragraph, the dynamometer and engine shall be returned to the idle condition described in subparagraph (1) of this paragraph.

(b) The procedures described in paragraph (a) (1) through (4) of this section shall be repeated until the entire cycle has been run three times.

TABLE C-1

GASEOUS EMISSION SUMMARY - 13-MODE CYCLE

DDAD 3-53 Engine - Fuel 2-16

Modal Data

Mode	RPM	Hp	% Load	Bsfc lb/BHP-Hr	Exh. Flow lb/hr	Fuel/Air[1] Ratio	Concentration, ppm				Mass, g/hr.				Smoke, % Opacity
							CO	NO_2	NO	HC	CO	NO_2	NO[2]	HC	
1	505	0.3	-	4.597	241	0.0054	263	28	139	190	27.6	4.5	21.9	10.0	0.6
2	1816	2.7	4.0	2.497	833	0.0083	325	29	128	271	116.8	15.6	68.8	50.2	0.5
3	1822	16.8	24.7	0.606	837	0.0123	238	45	222	240	85.1	24.1	118.6	44.7	0.6
4	1820	33.9	50.0	0.455	845	0.0186	213	80	407	238	76.1	43.0	218.0	44.9	0.8
5	1813	50.7	74.7	0.433	843	0.0268	400	149	633	250	140.6	78.8	335.7	47.0	2.5
6	1817	67.9	100.0	0.450	845	0.0375	5788	206	857	140	1992.1	108.6	448.2	26.7	14.2
7	500	0.2	-	6.180	240	0.0053	188	30	146	157	19.5	4.7	22.5	8.6	0.6
8	2807	86.9	100.0	0.466	1222	0.0343	1150	269	843	275	587.5	204.4	642.0	75.3	4.2
9	2797	65.0	74.8	0.484	1214	0.0266	250	165	618	275	126.7	125.7	470.6	74.5	2.0
10	2801	43.7	50.3	0.558	1206	0.0206	175	65	382	265	89.1	49.8	291.4	71.7	1.3
11	2795	21.9	25.2	0.815	1205	0.0150	175	47	230	266	89.9	35.8	176.4	72.0	1.0
12	2802	3.2	3.7	4.862	1209	0.0130	175	41	181	279	90.4	31.5	140.0	75.8	0.8
13	505	0.3	-	4.203	239	0.0050	188	34	136	190	19.5	5.2	20.8	10.3	0.6

13-Mode Cycle Average, g/BHP-Hr[3]

Bsfc	BHP	CO	NO_2	NO[2]	HC
0.5472	31.48	8.82	1.85	7.53	1.54

(1) Includes Scavenger Air.

(2) Calculated as NO_2.

(3) Calculated as Specified in Federal Register.